# Exact quantum mechanical reaction probabilities and rate constants for the isotopic collinear $H+H_2$ reactions

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Quantum mechanical calculations on three of the collinear $H+H_2$ reactions involving D-substitutions are presented and compared with each other and with previous calculations on the $H+H_2$ reaction itself. The energy at which the reaction probability becomes appreciable is well predicted by the vibrationally adiabatic model. The reaction probabilities at low energies ("tunneling") are larger than predicted by tunneling through one-dimensional barriers for motion along the reaction coordinate. The deviations of the exact rates from transition state theory with unit transmission coefficient and with transmission coefficients corrected for tunneling and nonclassical reflection are examined. Transition state theory including tunneling is usually very accurate (correct within 20% for rate constants); but the errors are much larger at temperatures below 300°K. Although the main use of the present results is for testing approximate models of reaction, not for comparison with laboratory experiments, it is interesting to note that the isotope effects are in rough agreement with the (noncollinear) experimental ones. The results are used to examine the general validity of treatments of the dynamics which separate effects due to the different modes of motion.

## INTRODUCTION

We have recently reported results of our studies of the exact[1-3] and approximate[1-5] collision dynamics of the collinear (1-PD)[6] exchange reaction

$$H+H_2 \rightarrow H_2+H \tag{1}$$

on an approximate but realistic potential energy surface. At this time we are reporting reaction probabilities and rate constants for the isotopically analogous collinear reactions (and their reverses)

$$D+D_2 \rightarrow D_2+D\,, \tag{2}$$

$$D+H_2 \rightarrow DH+H\,, \tag{3}$$

$$H+D_2 \rightarrow HD+D \tag{4}$$

studied by the same methods,[1-4,7] on the same potential energy surface.[3] Our motivation for these 1-PD studies has been discussed previously.[1-3] Another collision-theory treatment of the quantum dynamics of the collinear reactions (2)–(4) has been reported by Mortenson,[8,9] and Russell and Light[10] also used collision theory to study the quantum dynamics of Reactions (1), (4), the reverse of (3), and two other isotopic analogs of (1). Mortenson's calculations, like the present ones, are exact calculations of the collinear dynamics for an assumed potential surface; however, he has modified the potential surface from the collinear one to simulate the bent configurations which actually occur in 3-PD collisions.[6] The calculations of Russell and Light are, like the present calculations, for the strictly collinear collision but their calculations involve the assumption that the wavefunction can be accurately represented by the first term in its expansion in natural-collision-coordinate harmonic vibrational functions. Mortenson also performed transition state theory calculations for comparison with his collision theory ones and he also explicitly considered the reverse reactions.

No work has been done on the isotopically substituted $H+H_2$ reactions in 2-PD. There have been many transition state theory calculations on reactions (2)–(4)[11-25] and the other isotopically substituted $H+H_2$ reactions[12-16,18,24] in 3-PD. There have also been some 3-PD collision theory treatments of reactions (2)–(4)[26,27] and other isotopically substituted $H+H_2$ reactions.[28] However, calculations of accurate 3-PD quantum collision dynamics for a given potential surface are too expensive for any reaction at this time and all theoretical treatments of the 3-PD quantum dynamics have involved significant approximations.

It may be interesting to inject a historical note here. Collision theory as it was able to be used in practice before computers revolutionized chemical dynamics was quite simple and was unable to explain isotope effects properly. Thus, explanation of dynamical isotope effects was one of the great successes[11,12] for transition state theory. This article and Refs. 8–10 are examples of the resurgence of quantum collision theory and its new found ability to handle all the important questions of chemical dynamics.

TABLE I. Parameters for Eq. (5)–(7).

| | $\mu_i$ (aum)[a] | $W$ (eV × aum$^{1/2}$) | $X$ (eV × aum) | $\mu$ (aum) |
|---|---|---|---|---|
| $H_2$ | 919.0 | 16.785 | 14.941 | |
| HD | 1224.9[b] | | | |
| $D_2$ | 1836.2 | | | |
| HHH | 3676.2 | 15.248 | 14.765 | 1225.4 |
| DDD | 7344.8 | | | 2448.3 |
| DHH | 4957.9 | | | 1837.1 |
| HDD | 4967.9 | | | 1470.2 |

[a]aum = atomic mass unit. To convert to grams, multiply by $9.108 \times 10^{-28}$.

[b]Not necessary for present calculations (included for completeness).

## METHODS

The methods used for the exact probability of reaction and reaction rate calculations were the same as previously described in detail[3] for Reaction (1) except that a smaller step size $h$ was used in the finite difference grids. This was necessary to achieve comparable accuracy since the heavier masses result in smaller de Broglie wavelengths at the same collision energy. For most calculations, we used grids with 2025, 3025, and 4225 points and $h^4$ extrapolation. Examination of the Neville tables indicates[29] that the probability of reaction is usually accurate to better than 1%. The rate constants presented here are not quite as accurate but are probably accurate within a few percent at $T \geq 250$ °K. At $T = 200$ °K, the errors in the rate constants may be a little larger for reactions (1) and (3) but are still less than 10%.

The methods used for the approximate calculations are also essentially the same as previously described in detail[3] for Reaction (1). Calculations in 1-MD along appropriate cuts of the same potential energy surface and using the same finite difference approximation (including extrapolation to zero step size) as in the scattering calculations were performed to obtain the vibrational energies $E_n^v$ of $H_2$ and $D_2$ and for the symmetric-stretching-mode energies $E_n^{vs}$ of the $H_3$ and $D_3$ transition states. These calculations are approximately fit by

$$E_n = (n+1/2)\omega_e - (n+1/2)^2\omega_e x_e \,, \tag{5}$$

$$\omega_e = \mu_i^{-1/2} W \,, \tag{6}$$

$$\omega_e x_e = \mu_i^{-1} X \,, \tag{7}$$

where the reduced masses $\mu_i$ and the constants $W$ and $X$ are given in Table I. For the unsymmetrical transition states the normal modes of the transition state are different; in these cases we calculated an effective $\mu_i$ for the transition-state vibration using the harmonic approximation, i.e.,

$$\mu_i = (\nu_{H_3}^{vs} / \nu_i^{vs})^2 \mu_{H_3} \,, \tag{8}$$

where $\nu^{vs}$ are the harmonic frequencies for the transverse stretch of the transition state taken from Shavitt's Table I.[23] Then Eqs. (5)–(7) are used to calculate barrier heights in the vibrational adiabatic model and partition functions in the transition-state theory treatment. The reduced mass $\mu$ for relative motion of the reagents is also required for several of the calculations and is also given in Table I. The transition-state theory calculations for Reaction (1) are thus essentially the same as those reported in Refs. 2 and 3 and the calculations for Reaction (2) also follow this procedure. The only difference for Reaction (1) is the use of the exact $E_n$ instead of Eq. (5). The above transition-state theory treatment however corresponds to an approximate treatment of the anharmonicity of the vibration of the transition state for Reactions (3) and (4). Since anharmonicity itself is a small correction, we feel this is an adequate treatment.

We use the exact rates $k_r(T)$ and the transition-state theory rates $k_{TST}(T)$ to compute an "exact transmission coefficient"[2,3,8,9,30] for transition state theory from

$$\kappa(T) = k_r(T)/k_{TST}(T) \,. \tag{9}$$

From the exact rates $k_r(T)$ we computed the "exact" Arrhenius parameters by fitting the results to

$$k_r(T) = A \exp(-E_a/kT) \tag{10}$$

in different temperature ranges. For the fits we used a version of the least squares program ACTEN[31] which was modified for the CDC 6600. The input data for this program were the rate constants as a function of $T$ in steps of 50 °K. The relative error of each rate constant was assumed to be the same.

## RESULTS

The calculated exact results for the probabilities of reaction as functions of initial relative translational energy $E_0$ for ground vibrational state reagents are given in Figs. 1 and 2. For comparison, these figures also show the results for $H + H_2$. The total energies are related to $E_0$ by

$$E = E_0 + E_0^v \,, \tag{11}$$

where $E_0^v$ is 0.2728 eV for $H_2$ reagent and 0.1938 eV for $D_2$. These calculations are mainly for energies below the thresholds for vibrational excitation of reagents and products.

For Reactions (3) and (4) some calculations were carried out at energies above the vibrational excitation thresholds. The probability matrices for these cases and for one additional case below the thresholds are given in Tables II and III.

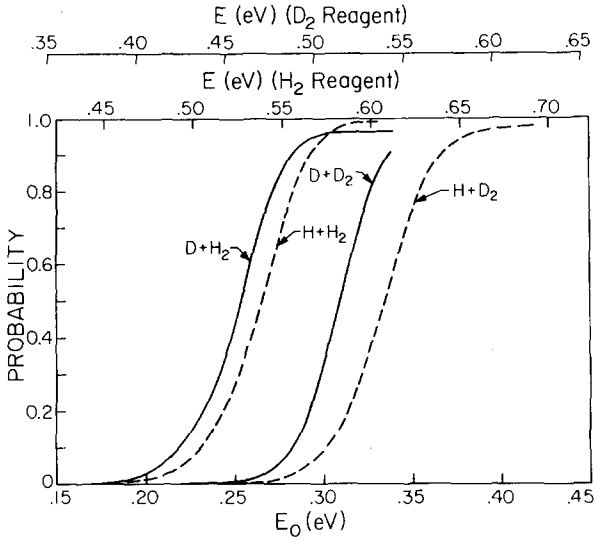


FIG. 1. Probability of reaction vs translational energy $E_0$ and total energy E for Reactions (1)–(4) with ground-state reagents.

The rate constants calculated from the probabilities are given in Table IV. The best-fit Arrhenius parameters for the collinear reactions (1)–(4) were calculated for three temperature regions: (a) the 250–750 °K region for which recent experimental data[21,22,24] on the 3-PD reaction is available, (b) the 200–1250 °K region considered in Refs. 2, 3, and 23, and (c) the 750–1250 °K region in which the Arrhenius plot is approximately a straight line. These parameters are given in Table V.

The exact transmission coefficients computed from Eq. (9) are given in Table VI.

## DISCUSSION

### A. Analysis of Exact Results

The probability of reaction curves for Reactions (1)–(4) have qualitatively the same shape but differ in the steepness of the rise and position of the rise. The steepness of the rise might be expected to correlate with the quantum effects on the reaction coordinate (i.e., with the likelihood of tunneling and nonclassical reflection of systems moving along the lowest energy reaction path) and the position of the rise might be expected to correlate with energy release into the reaction coordinate motion due to vibrational adiabaticity of the motion transverse to the reaction coordinate but, as first pointed out by Marcus,[32,33] the same energy release phenomenon will occur in a classical vibrationally

TABLE II. Scattering probabilities for ground state $D+H_2$ [Reaction (3)] at total energies $E$ too large to be shown in Fig. 2.

| | | Probability | | |
|---|---|---|---|---|
| | | Final vibrational quantum number | | |
| $E$ | $E_0$[a] | $D+H_2$ | DH+H | |
| (eV) | (eV) | 0 | 0 | 1 |
| 0.6600 | 0.3872 | 5.17(−2)[b] | 9.48(−1) | c |
| 0.7128 | 0.4400 | 7.91(−2) | 9.16(−1) | 4.6(−3) |

[a]Initial relative translational energy.
[b]Numbers in parentheses are powers of 10 by which preceding numbers should be multiplied.
[c]This channel closed at this energy.

TABLE III. Scattering probabilities for ground state $H+D_2$ [reaction (4)] at total energies $E$ above the threshold for vibrational excitation.

| | | Probability | | | |
|---|---|---|---|---|---|
| | | Final vibrational quantum number | | | |
| $E$ | $E_0$[a] | $H+D_2$ | | HD+D | |
| (eV) | (eV) | 0 | 1 | 0 | 1 |
| 0.5660 | 0.3722 | 7.39(−2)[b] | 2.7 (−4) | 9.26(−1) | 3.6(−4) |
| 0.5804 | 0.3866 | 3.13(−2) | 6.6 (−3) | 9.62(−1) | 9.0(−3) |
| 0.6100 | 0.4162 | 1.02(−2) | 8.3 (−3) | 9.81(−1) | 8.6(−3) |
| 0.6456 | 0.4518 | 6.5 (−3) | 9.6 (−3) | 9.84(−1) | 9.2(−3) |
| 0.7108 | 0.5170 | 1.16(−2) | 2.11(−2) | 9.62(−1) | 5.1(−3) |
| 0.7580 | 0.5642 | 8.39(−2) | 1.08(−1) | 8.00(−1) | 8.6(−3) |

[a]Initial relative translational energy.
[b]Numbers in parentheses are powers of 10 by which preceding numbers should be multiplied.

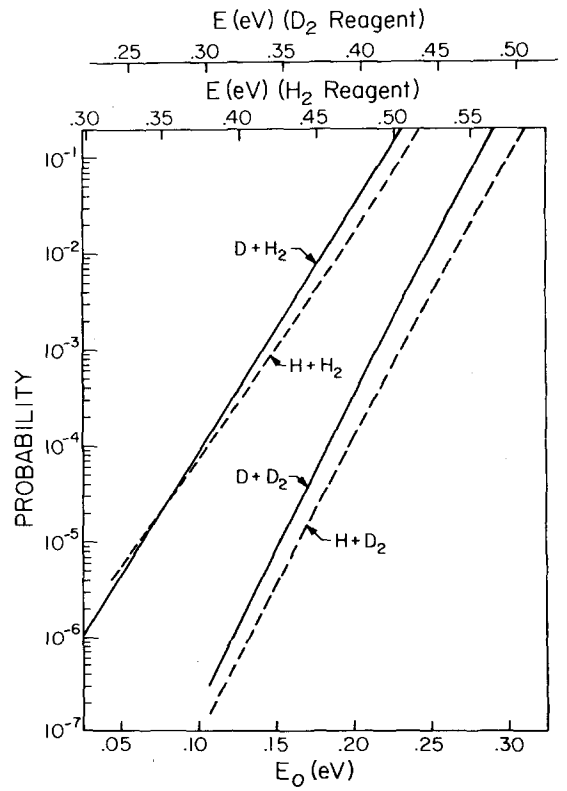


FIG. 2. Probability of reaction vs translational energy $E_0$ and total energy E for Reactions (1)–(4) with ground state reagents.

TABLE IV. Rate constants $k_r(T)$ for the collinear Reactions (1) to (4) in cm/molec × sec).

| | $k_r(T)$ | | | |
|---|---|---|---|---|
| $T$(°K) | $H+H_2$ (1) | $D+D_2$ (2) | $D+H_2$ (3) | $H+D_2$ (4) |
| 200 | 2.07(−1)[a] | 2.68(−3) | 2.14(−1) | 1.27(−3) |
| 250 | 1.19(0) | 5.97(−2) | 1.44 | 3.05(−2) |
| 300 | 5.87(0) | 5.54(−1) | 7.25 | 3.17(−1) |
| 350 | 2.13(1) | 2.88 | 2.54(+1) | 1.81 |
| 400 | 5.93(1) | 1.02(+1) | 6.82(+1) | 6.93 |
| 500 | 2.65(2) | 6.20(+1) | 2.87(+1) | 4.75(+1) |
| 650 | 1.13(3) | 3.45(+2) | 1.14(+3) | 2.96(+2) |
| 800 | 2.92(3) | 1.04(+3) | 2.81(+3) | 9.60(+2) |
| 900 | 4.66(3) | 1.79(+3) | 4.39(+3) | 1.71(+3) |
| 1000 | 6.84(3) | 2.78(+3) | 6.31(+3) | 2.73(+3) |
| 1100 | 9.42(3) | 4.00(+3) | 8.55(+3) | 4.01(+3) |
| 1200 | 1.24(4) | 5.45(+3) | 1.10(+4) | 5.56(+3) |
| 1250 | 1.40(4) | 6.25(+3) | 1.24(+4) | 6.43(+3) |

[a]Numbers in parentheses are powers of 10 by which preceding numbers should be multiplied.

TABLE VI. "Exact transmission coefficients" as defined in Eq. (9) for Reactions (1)–(4).

| $T$(°K) | (1) $H+H_2$ | (2) $D+D_2$ | (3) $D+H_2$ | (4) $H+D_2$ |
|---|---|---|---|---|
| 200 | 29.79 | 6.47 | 13.84 | 7.15 |
| 250 | 6.13 | 3.20 | 4.16 | 3.05 |
| 300 | 3.30 | 2.30 | 2.57 | 2.12 |
| 350 | 2.41 | 1.89 | 2.00 | 1.74 |
| 400 | 2.00 | 1.67 | 1.71 | 1.53 |
| 450 | 1.77 | 1.52 | 1.54 | 1.41 |
| 500 | 1.61 | 1.41 | 1.42 | 1.32 |
| 600 | 1.43 | 1.27 | 1.28 | 1.21 |
| 700 | 1.31 | 1.17 | 1.19 | 1.13 |
| 800 | 1.23 | 1.10 | 1.12 | 1.07 |
| 900 | 1.17 | 1.04 | 1.06 | 1.03 |
| 1000 | 1.12 | 0.99 | 1.02 | 0.99 |
| 1100 | 1.08 | 0.95 | 0.98 | 0.96 |
| 1200 | 1.04 | 0.91 | 0.94 | 0.93 |
| 1250 | 1.02 | 0.90 | 0.92 | 0.91 |

adiabatic system as in a quantum vibrationally adiabatic one. However, such a separation of the two features is not strictly possible since the two modes of motion (along the reaction coordinate and transverse to it) are not strictly separable. Therefore it is interesting to see how good an approximation it is to separately correlate these two features to effects associated with these two modes.

The results show roughly that a larger imaginary frequency of the asymmetric stretch normal mode of the transition state means a less steep rise of the $P^R$ curve. Thus, e.g., $H_3$ is less steep than $D_3$. This comparison is shown in Table VII. Another example, seen in Fig. 1, is that $D+H_2$ and $H+H_2$ are less steep at low $E_0$ than are $D+D_2$ and $H+D_2$. This direction of the effect is in agreement with the direction expected due to tunneling and nonclassical reflection along the reaction coordinate. However, Table VII shows it is not a complete explanation. Another factor affecting the steepness is the curvature of the reaction path.[34,35] Marcus found that such curvature effects (sometimes called "centrifugal effects" by him) lead to an effective raising of the barrier at energies where the reaction probability is below about 0.5 and an effective lowering of the barrier at higher energies.[34] Russell and Light similarly concluded that "Reaction path curvature effects are such that at low incident energies the reaction probability is decreased while at high incident energies the effects are just the opposite."[10] Although the curvature of the minimum energy reaction path on the classical potential energy surface is the same for all isotopic variations of a reaction, the effective curvature is a dynamical quantity which depends

TABLE V. Exact Arrhenius parameters.

| Reactants | $T$ range (°K) | $A$ [cm/molec × sec)] | $E_a$ (eV/molec) |
|---|---|---|---|
| | 250–750 | 8.75(4)[a] | 0.247[b] |
| (1) $H+H_2$ | 200–1250 | 9.60(4) | 0.241 |
| | 750–1250 | 2.12(5) | 0.296 |
| | 250–750 | 7.96(4) | 0.306 |
| (2) $D+D_2$ | 200–1250 | 7.80(4) | 0.303 |
| | 750–1250 | 1.31(5) | 0.342 |
| | 250–750 | 7.66(4) | 0.238 |
| (3) $D+H_2$ | 200–1250 | 8.50(4) | 0.235 |
| | 750–1250 | 1.68(5) | 0.282 |
| | 250–750 | 9.43(4) | 0.324 |
| (4) $H+D_2$ | 200–1250 | 1.06(5) | 0.324 |
| | 750–1250 | 1.86(5) | 0.363 |

[a]Numbers in parentheses are powers of 10 by which preceding numbers should be multiplied.

[b]1 eV/molec = 23.069 kcal/mole.

TABLE VII. Comparison of relative translational energies $E_0^x$ (in eV) at which the reaction probabilities become $x$ with the imaginary frequency $\nu$ associated with the reaction coordinate normal mode of the transition state.

| Reaction | $E_0^{0.01}$ | $E_0^{0.1}$ | $E_0^{0.9}$ | $E_0^{0.9}-E_0^{0.01}$ | $E_0^{0.9}-E_0^{0.1}$ | $h\nu$[a] (eV) |
|---|---|---|---|---|---|---|
| (1) $H+H_2$ | 0.190 | 0.231 | 0.295 | 0.105[b] | 0.064[b] | $0.181i$ |
| (2) $D+D_2$ | 0.248 | 0.2813 | 0.3363 | 0.088 | 0.055 | $0.128i$ |
| (3) $D+H_2$ | 0.181 | 0.219 | 0.285 | 0.104 | 0.066 | $0.172i$ |
| (4) $H+D_2$ | 0.266 | 0.3015 | 0.3702 | 0.104 | 0.069 | $0.136i$ |

[a]From Table II of Ref. 23.

[b]The numbers in these columns are inversely related to the steepness of the rise of the probability of reaction vs $E$ curve.

TABLE VIII. Initial vibrational energies ($E_0^V$), barrier heights in VAZC approximation ($E^{VAZC}$), and $E_0^{0.5}$ (the relative translational energy at which the probability of reaction equals 0.5).

| Reagents | $E_0^V$ (eV) | $E^{VAZC}$ (eV) | $E_0^{0.5}$ (eV) |
|---|---|---|---|
| (1) H + $H_2$ | 0.273 | 0.28 | 0.27 |
| (2) D + $D_2$ | 0.194 | 0.32 | 0.31 |
| (3) D + $H_2$ | 0.273 | 0.26 | 0.25 |
| (4) H + $D_2$ | 0.194 | 0.34 | 0.34 |

on the masses.[36] Thus Russell and Light found that curvature effects are more pronounced in the H transfer reactions than in D transfer.[10] A qualitative explanation of the differences in steepness of the rise of the reaction probability curves for the different reactions therefore requires at least including these two aspects of reaction coordinate motion.

The second question is whether release of vibrational energy from the vibrational mode as the vibrational valley in the potential surface widens near the transition state is the main consideration for determining the differences in the positions of the rises of the reaction probability curves for reactions (1)–(4). We will use the vibrationally adiabatic zero-curvature (VAZC) model[1,3,34–36] to study this question. In this case the barrier height $E^{VAZC}$ is the classical barrier height minus the difference in zero-point energies of the reactant and the vibrational mode of the transition state which is transverse to the reaction path. This VAZC barrier height is compared in Table VIII to the energy $E_0^{0.5}$ at which the probability of reaction is 0.5. The agreement is remarkably good since the trends are predicted within 0.01 eV. For contrast the table also compares $E_0^{0.5}$ to the initial vibrational energy of the reagent. The trends show that the VAZC model correlates the data much better than the assumption that an approximately constant fraction of the vibrational energy is released.

Mortensen[8] also found a good correlation of $E^{VAZC}$ and $E_0^{0.5}$. In his case the quantity $E^{VAZC} - E_0^{0.5}$ was in the range 0.016–0.040 eV for Reactions (1)–(4) and thus the trends were predicted within 0.024 eV. Russell and Light[10] found $E^{VAZC} - E_0^{0.5}$ was about 0.005 eV for Reaction (1) and about 0.00 eV for Reaction (4) and thus our exact quantum mechanical results for this quantity for four strictly collinear reactions are in excellent agreement with their results for the two reactions which both studies have in common.

In their conclusions, Russell and Light[10] state that since the inclusion of vibrational energy release effects will increase the reaction probability in quantum 1-MD tunneling calculations, it will always increase the "tunneling corrections" computed for transition state theory. Actually this is not true. The quantum 1-MD tunneling calculation does enter the numerator of the tunneling correction but calculations including and not including such effects use different formalisms (called VA and CVE, respectively) involving different denominators (as well as different numerators) in the tunneling correction. This point was discussed extensively by us[4] earlier.

Comparison of $E^{VAZC}$ in Table VIII with $E_a$ in Table V shows good correlation between these quantities, especially for the fits to the higher temperature data. For the Arrhenius fits in the 750–1250 °K range, $E^{VAZC} - E_a$ is 0.02 eV. It is usually assumed by careful workers that experimental determinations of $E_a$ measure approximately $E^{VAZC}$ because[37] transition-state theory leads approximately to this result. The present calculations show strikingly that collision theory also leads approximately to this result for the reactions considered.

It is interesting to compare the three different sets of Arrhenius parameters. Quite different results are obtained for the best-fit Arrhenius parameters when only the high-temperature results are included than when the low-temperature results are included. Experimental rate constants are not usually determined by one technique over as large a range (1050 °K) as considered here and thus it is not easy to show this sensitivity to Arrhenius parameters to the temperature range from experimental data. The present results show that one must be extremely cautious about comparing Arrhenius parameters determined in different temperature ranges. In particular, the differences among the $E_a$ are very large compared to what is commonly given as "chemical accuracy," viz., 1 kcal/mole (which equals 0.04 eV).

The present study of isotopically substituted reactions does not include enough calculations on vibrationally excited species for a detailed analysis of the results. The few which we have obtained (see Tables II and III) mainly show the following: (a) The total probability of reaction after rising to very near 1 drops as the energy is further increased. (The average total probability of reaction in our seven calculations above the threshold for vibrational excitation of the product is 0.94.) (b) The probability of vibrational excitation is fairly low at energies not too far past the threshold. (The average probability of reaction into a vibrationally excited state for the seven calculations where this is energetically allowed is only 0.0065.)

### B. Comparison with Transition-State Theory

In transition-state theory one assumes the motion along the reaction coordinate is separable.

Then the vibrational adiabatic derivation of transition state theory leads to the following expression for the transmission coefficient[3,4,38,39]

$$\kappa_{TST}(T) = \sum_n \kappa(T,n) \exp\left(-\frac{E_n^{vs}}{kT}\right) \Big/ \sum_n \exp\left(-\frac{E_n^{vs}}{kT}\right), \tag{12}$$

where

$$\kappa(T,n) = (kT)^{-1} \int_{-\infty}^{\infty} dE_{tr,n}^{+} \exp(-E_{tr,n}^{+}/kT) P_n^R(E_{tr,n}^{+}) . \tag{13}$$

$P_n^R$ is the probability of reaction of a particle moving along the one-dimensional vibrational adiabatic barrier $V_n^{VA}(s)$, $s$ is the reaction coordinate, $n$ is the initial vibrational quantum number, $E_n^{VA}$ is the energy of the vibrational adiabatic barrier at the transition state, $E$ is the total energy and

$$E_{tr,n}^{+} = E - E_n^{VA} ; \tag{14}$$

i.e., $E_{tr,n}^{+}$ is the translational energy at the transition state if the reaction is vibrationally adiabatic. $E$ and $E_n^{VA}$ must be measured with respect to the same reference configuration, taken as the minimum of the potential energy surface for the separated reagents. (The height of the vibrational adiabatic barrier is $E_n^{VA} - E_n^v$, where $E_n^v$ is the energy of the $n$th vibrational state of the isolated molecular reagent.) $V_n^{VA}(s)$ is obtained by adding to the potential energy along the reaction coordinate $V(s)$ the energy of the $n$th vibrational state of the transverse mode motion at $s$. We computed transmission coefficients for Reaction (2) by making the usual approximation

$$\kappa_{TST}(T) \cong \kappa(T,0) \tag{15}$$

and using the type of model usually used for $\kappa(T, 0)$, viz., calculating it from 1-MD reaction probabilities for assumed potential energy barriers which approximately or accurately represent the classical potential energy as a function of $s$ (for discussion of this type of model, see Ref. 4 where it is referred to as the conservation-of-vibrational-energy approximation; in the present article we just consider the result of this usual type of treatment empirically. We will not present again our criticisms of this model according to which the vibrationally adiabatic barrier is the theoretically most consistent one to use in transition state theory). Three 1-MD models are considered: (a) Shavitt's truncated Eckart barrier fit to the classical potential energy barrier along the minimum-energy path, (b) the usual Eckart barrier fit to this barrier (which involves fitting the height of the barrier and the curvature at the top to the height of the classical potential energy barrier and to the curvature at the top of the classical potential energy barrier along the asymmetric stretch normal mode, respectively), and (c) the actual classical potential energy barrier along the minimum-energy path. For each of these three barriers the exact 1-MD reaction probabilities were computed numerically and the transmission coefficient was computed in the usual way,[4] viz., using (15) and (13) with

$$E_{tr,n}^{+} = E_n - E^{CVEZC} \tag{16}$$

instead of (14). In (16), $E^{CVEZC}$ is the classical barrier height (0.424 eV). The results are given in Table IX. Again the calculated transmission coefficients are in all cases larger than the exact ones obtained from Eq. (9). Further comparison of Tables VI and IX shows that at temperatures of 400 °K and higher these calculations are all accurate within 22%. However, at temperatures below 400 °K they are worse, e.g., at 200 °K, calculation (c) is in error by a factor of 2.22. Thus the combination of transition-state theory with the usual type of transmission coefficient fails badly for the $D + D_2$ reaction when this calculated transmission coefficient becomes greater than about 2. This should be a warning of possible inaccuracies in the treatment of experimental data in cases where a large transmission coefficient is calculated.

### C. Comparison of Rate Ratios with 3-PD Experiments

Westenberg and de Haas have pointed out[22,40] that

$$\frac{d^2}{dT^2} \log\left(\frac{k_3(T)}{k_4(T)}\right)$$

as determined by their experiments on Reactions

TABLE IX. Some 1-MD transmission coefficients for $D + D_2$ [reaction (2)] in the CVEZC model (c) and two approximations to it [(a) and (b)]. The last row is the average deviation of each column from the exact empirical results in Table VI.)

| $T$ | Transmission coefficient | | |
|---|---|---|---|
| (deg) | (a) | (b) | (c) |
| 200 | 10.24 | 24.45 | 14.39 |
| 250 | 4.52 | 6.09 | 4.89 |
| 300 | 2.91 | 3.26 | 2.95 |
| 350 | 2.23 | 2.33 | 2.21 |
| 400 | 1.88 | 1.90 | 1.85 |
| 450 | 1.66 | 1.65 | 1.63 |
| 500 | 1.53 | 1.50 | 1.50 |
| 600 | 1.36 | 1.33 | 1.33 |
| 700 | 1.27 | 1.24 | 1.24 |
| 800 | 1.21 | 1.18 | 1.19 |
| 900 | 1.17 | 1.14 | 1.15 |
| 1000 | 1.14 | 1.12 | 1.12 |
| 1100 | 1.12 | 1.10 | 1.11 |
| 1200 | 1.10 | 1.08 | 1.09 |
| 1250 | 1.10 | 1.08 | 1.08 |
| av.% deviation | 19 | 37 | 23 |

(3) and (4) is negative while all tunneling theories predict it to be of the opposite sign. Figure 3 presents a comparison of their experimental data for the ratio of reaction rates of reactions (3) and (4) in 3-PD and the present exact results for this ratio in 1-PD. The logarithm of the 1-PD ratio can be fit very well to a straight line above 500 °K. This straight line fit extrapolates to $k_3/k_4 = 29$ at 275 °K, while the exact 1-PD ratio at this temperature is 32. Thus the 1-PD ratio has a positive second derivative and the experiment is still unexplained. Because of the many differences in the 1-PD and 3-PD reactions it is hard to attribute the difference to some dominant factor. Nevertheless the comparison is intriguing since almost all attempts to interpret such 3-PD data have involved 1-PD tunneling corrections. The comparison shows that a *full* 1-PD calculation does contain some qualitative features of the experiment but does not explain the experimental curvature. The explanation of this curvature thus requires including features which are not contained in a 1-PD model. The figure also compares the present results with the

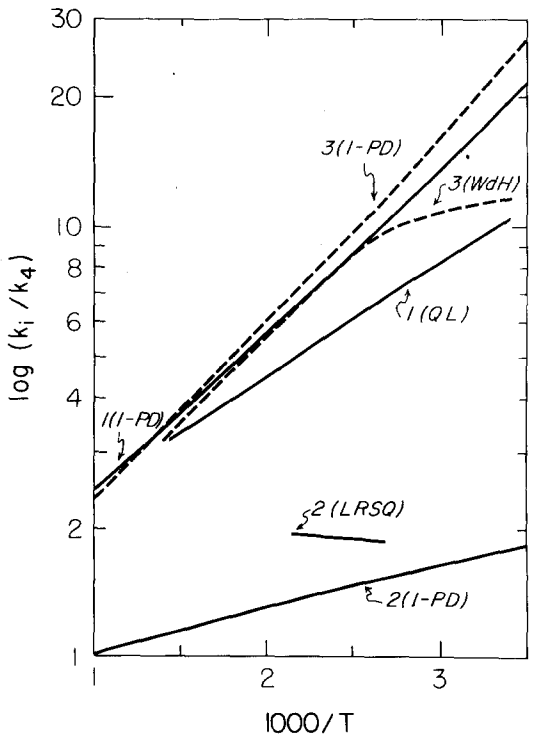


FIG. 3. Ratio ($k_i/k_4$) of rate constants for reactions $i=1$, 2, and 3 to the rate constant for Reaction 4 ($H+D_2$). For $i=1$ ($H+H_2$), comparison is made with the experiments of Quickert and LeRoy (Ref. 24). For $i=2$ ($D+D_2$), comparison is made with the experiments of LeRoy, Ridley, Schultz, and Quickert (as summarized in Ref. 21). For $i=3$ ($D+H_2$), comparison is made with the experiments of Westenberg and de Haas (Ref. 22).

TABLE X. Low-temperature rate ratios.

| $T$ (k) | 1000 $k/T$ | $k_1/k_4$ | $k_2/k_4$ | $k_3/k_4$ |
|---|---|---|---|---|
| 300 | 3.33 | 18.5 | 1.75 | 22.9 |
| 250 | 4.00 | 38.5 | 1.96 | 47.4 |
| 200 | 5.00 | 163. | 2.11 | 168. |

best available experimental data for the ratios $k_1/k_4$ (Ref. 24) and $k_2/k_4$ (Ref. 21). There is qualitative agreement as to the magnitudes but poor agreement for the temperature dependence. Since the temperature dependence is dominated by a factor equal approximately to $\exp(-E^{VA}/kT)$ and $E^{VA}$ is quite different in 1-PD and 3-PD, the latter discrepancy is not unexpected. Table X shows the three sets of computed ratios in the temperature range just lower than shown in Fig. 3 (there is no experimental data for the 3-PD reaction in this temperature range). An interesting feature of these results is that the rates of Reactions (1) and (3), which involve hydrogen-atom transfer, become very much larger than Reactions (2) and (4), which involve deuterium-atom transfer, at low relative translational energies. It is possible that such a large effect could be observed in the 3-PD reaction if experiments were carried out at a low enough temperature.

## FINAL REMARKS

The present article has dealt with the exact probabilities of reaction in 1-PD and the associated rate constants. We compared these results to 3-PD experiments and used them to discuss the general validity of treatments which separate the modes of motion (such as, but not only, transition state theory). However, a fuller analysis of these results requires a more detailed study of the wavefunctions. The reaction probabilities (and rate constants) involve examination of only the asymptotic part of the exact wavefunction. Many theories of the reactions can be tested in detail by studying the rest of the wavefunction. We have studied the wavefunctions for reaction (1) from this point of view and will present the results of these studies soon.[41]

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[1]D. G. Truhlar and A. Kuppermann, J. Chem. Phys. **52**, 3841 (1970).
[2]D. G. Truhlar and A. Kuppermann, Chem. Phys. Lett. **9**, 269 (1971).
[3]D. G. Truhlar and A. Kuppermann, J. Chem. Phys. **56**, 2232

(1972).
[4]D. G. Truhlar and A. Kuppermann, J. Am. Chem. Soc. **93,** 1840 (1970).
[5]J. Bowman and A. Kuppermann, Chem. Phys. Lett. **12,** 1 (1971).
[6]We study collinear reactions in the two-mathematical-dimensional (2-MD) coordinate systems which result after separating the center–of–mass motion out of the problem of three particles on a line. The three particles on a line are in one physical dimension (1-PD). A full treatment of the 3-PD reaction involves six-mathematical dimensional (6-MD). coordinate systems after separating out the center–of–mass motion.
[7]D. J. Diestler and V. McKoy, J. Chem. Phys. **48,** 2951 (1968).
[8]E. M. Mortenson, J. Chem. Phys. **48,** 4029 (1968).
[9]E. M. Mortenson, J. Chem. Phys. **49,** 3526 (1968).
[10]J. D. Russell and J. C. Light, J. Chem. Phys. **54,** 4881 (1971). To compare this article to our Ref. 3 and to the present article, note that their $\bar{V}(s)$ is the VA barrier in our notation, their $\bar{V}'(s)$ is the CVE barrier, their $\bar{V}''(s)$ is the VAZC barrier, and their $E^*$ is the VAZC barrier height.
[11]L. Farkas and E. Wigner, Trans. Faraday Soc. **32,** 708 (1936).
[12]J. Hirschfelder, H. Eyring, and B. Topley, J. Chem. Phys. **4,** 170 (1936).
[13]M. van Meersche, Bull. Soc. Chim. Belg. **60,** 99 (1951).
[14]R. E. Weston, J. Chem. Phys. **31,** 892 (1959).
[15]I. Shavitt, J. Chem. Phys. **31,** 1359 (1959).
[16]G. Boats, G. Caren, A. Cimono, E. Molenari, and G. G. Volpi, J. Chem. Phys. **24,** 783 (1956).
[17]H. S. Johnston and D. Rapp, J. Am. Chem. Soc. **83,** 1 (1961).
[18]See also D. Rapp and R. E. Weston, J. Chem. Phys. **36,** 2807 (1962); D. M. Bishop and K. J. Laidler, J. Chem. Phys. **42,** 1688 (1965).
[19]H. S. Johnston, *Gas Phase Reaction Rate Theory* (Ronald, New York, 1966).
[20]B. A. Ridley, W. R. Schulz, and D. J. LeRoy, J. Chem. Phys. **44,** 3344 (1966).
[21]D. J. LeRoy, B. A. Ridley, and K. A. Quickert, Discuss. Faraday Soc. **44,** 92 (1968).
[22]A. A. Westenberg and N. de Haas, J. Chem. Phys. **47,** 1393 (1967).
[23]I. Shavitt, J. Chem. Phys. **49,** 4048 (1968).
[24]K. A. Quickert and D. J. LeRoy, J. Chem. Phys. **53,** 1325 (1970); J. Chem. Phys. **54,** 5444 (1971).
[25]See also A. Tweedale and K. H. Laidler, J. Chem. Phys. **53,** 2045 (1970).
[26]M. Karplus, R. N. Porter, and R. D. Sharma, J. Chem. Phys. **40,** 2033 (1964).
[27]D. A. Micha, Ark. Fys. **30,** 437 (1965).
[28]M. Karplus, R. N. Porter, and R. D. Sharma, J. Chem. Phys. **45,** 3871 (1966).
[29]Some verification that this is a reliable way to determine the approximate accuracy of the calculations is given in Ref. 3, and even more conclusive verification is given in D. J. Diestler, D. G. Truhlar, and A. Kuppermann, Chem. Phys. Lett. **13,** 1 (1972).
[30]M. Karplus, R. N. Porter, and R. D. Sharma, J. Chem. Phys. **43,** 3259 (1965).
[31]Available as program number 179 from Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, IN 47401.
[32]R. A. Marcus, J. Chem. Phys. **43,** 1598 (1965).
[33]See also R. A. Marcus, Discuss. Faraday Soc. **44,** 7 (1968).
[34]R. A. Marcus, J. Chem. Phys. **49,** 2617 (1969). See also R. A. Marcus, J. Chem. Phys. **41,** 610 (1967); J. Chem. Phys. **45,** 4500 (1966).
[35]R. A. Marcus, J. Chem. Phys. **45,** 4493 (1966).
[36]R. E. Wyatt, J. Chem. Phys. **51,** 3489 (1969).
[37]See, e.g., Ref. 18.
[38]J. O. Hirschfelder and E. P. Wigner, J. Chem. Phys. **7,** 616 (1939).
[39]R. A. Marcus, J. Chem. Phys. **46,** 959 (1967).
[40]A. A. Westenberg and N. de Haas, J. Chem. Phys. **47,** 4241 (1967).
[41]Some of these results are reported in J. M. Bowman, A. Kuppermann, J. T. Adams, and D. G. Truhlar, Chem. Phys. Lett. (to be published).